



11. ☒ Please see the attached Preliminary Amendment
12. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)), i.e., before 18th month from first priority date above in item 3, are transmitted herewith (file only if in English) including:
13. ☒ PCT Article 19 claim amendments (if any) have been transmitted by the International Bureau
14. ☐ Translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)), i.e., of claim amendments made before 18th month, is attached (required by 20th month from the date in item 3 if box 4(a) above is X'd, or 30th month if box 4(b) is X'd, or else amendments will be considered canceled).
15. **A declaration of the inventor** (35 U.S.C. 371(c)(4))  
 a. ☐ is submitted herewith ☐ Original ☐ Facsimile/Copy  
 b. ☒ is not herewith, but will be filed when required by the forthcoming PTO Missing Requirements Notice per Rule 494(c) if box 4(a) is X'd or Rule 495(c) if box 4(b) is X'd.
16. **An International Search Report (ISR):**  
 a. Was prepared by ☒ European Patent Office ☐ Japanese Patent Office ☐ Other  
 b. ☒ has been transmitted by the international Bureau to PTO.  
 c. ☐ copy herewith ( ☐ pg(s). ) ☐ plus Annex of family members ( ☐ pg(s) ).
17. **International Preliminary Examination Report (IPER):**  
 a. ☒ has been transmitted (if this letter is filed after 28 months from date in item 3) in English by the International Bureau with Annexes (if any) in original language.  
 b. ☐ copy herewith in English.  
 c.1 ☐ IPER Annex(es) in original language ("Annexes" are amendments made to claims/spec/drawings during Examination) including attached amended:  
 c.2 ☐ Specification/claim pages # ☐ claims # ☐  
 Dwg Sheets # ☐  
 d. ☐ Translation of Annex(es) to IPER (required by 30<sup>th</sup> month due date, or else annexed amendments will be considered canceled).
18. **Information Disclosure Statement** including:  
 a. ☒ Attached Form PTO-1449 listing documents  
 b. ☒ Attached copies of documents listed on Form PTO-1449  
 c. ☒ A concise explanation of relevance of ISR references is given in the ISR.
19. ☐ **Assignment** document and Cover Sheet for recording are attached. Please mail the recorded assignment document back to the person whose signature, name and address appear at the end of this letter.
20. ☐ Copy of Power to IA agent.
21. ☐ **Drawings** (complete only if 8d or 10a(4) not completed): ☐ sheet(s) per set: ☐ 1 set informal; ☐ Formal of size ☐ A4 ☐ 11"
22. Small Entity Status ☒ is **Not** claimed ☐ is claimed (pre-filing confirmation required)
- 22(a) ☐ (No.) Small Entity Statement(s) enclosed (since 9/8/00 Small Entity Statements(s) not essential to make claim)
23. **Priority** is hereby claimed under 35 U.S.C. 119/365 based on the priority claim and the certified copy, both filed in the International Application during the international stage based on the filing in (country) Great Britain of:  

|     | Application No. | Filing Date    |     | Application No. | Filing Date |
|-----|-----------------|----------------|-----|-----------------|-------------|
| (1) | 9918782.5       | 10 August 1999 | (2) |                 |             |
| (3) |                 |                | (4) |                 |             |
| (5) |                 |                | (6) |                 |             |

 a. ☒ See Form PCT/IB/304 sent to US/DO with copy of priority documents. If copy has not been received, please proceed promptly to obtain same from the IB.  
 b. ☐ Copy of Form PCT/IB/304 attached.

RE: USA National Phase Filing of PCT/GB00/02785

24. Attached:

25 Per Item 17.c, **cancel original** pages #\_\_\_, claims #\_\_\_, Drawing Sheets #

26. **Calculation of the U.S. National Fee (35 U.S.C. 371 (c)(1)) and other fees is as follows:**

Based on amended claim(s) per above item(s) ☐ 12, ☐ 14, ☐ 17, ☐ 25 (hilitte)

|  |    |            |   |                 |   |       |         |
|--|----|------------|---|-----------------|---|-------|---------|
| Total Effective Claims   | 22 | minus 20 = | 2 | x \$18/\$9      | = | \$36  | 966/967 |
| Independent Claims   | 7  | minus 3 =  | 4 | x \$84/\$42     | = | \$336 | 964/965 |
| If any proper (ignore improper) Multiple Dependent claim is present, |    |            |   | add \$280/\$140 | + | 0     | 968/969 |

BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(4)): → → **BASIC FEE REQUIRED, NOW** → → →

A. If country code letters in item 1 are **not** "US", "BR", "BB", "TT", "MX", "IL", "NZ", "IN" or "ZA"

See item 16 re:

|  |                      |         |
|--|----------------------|---------|
| 1. Search Report was <u>not prepared</u> by EPO or JPO ----- | add \$1,040/\$520    | 960/961 |
| 2. Search Report was prepared by EPO or JPO -----            | add \$890/\$445 +890 | 970/971 |

**SKIP B, C, D AND E UNLESS country code letters in item 1 are "US", "BR", "BB", "TT", "MX", "IL", "NZ", "IN", "ZA", "LC" or "PH"**

|  |                   |    |         |
|--|-------------------|----|---------|
| → <input type="checkbox"/> B. If USPTO did not issue both International Search Report (ISR) and (if box 4(b) above is X'd) the International Examination Report (IPER), -----  | add \$1,040/\$520 | +0 | 960/961 |
| (only) → <input type="checkbox"/> C. If USPTO issued ISR but not IPER (or box 4(a) above is (one) X'd), -----  | add \$740/\$370   | +0 | 958/959 |
| (these) → <input type="checkbox"/> D. If USPTO issued IPER but IPER Sec. V boxes <u>not all</u> 3 (boxes) YES, -----   | add \$710/\$355   | +0 | 956/957 |
| → <input type="checkbox"/> E. If international preliminary examination fee was paid to USPTO and Rules 492(a)(4) and 496(b) <u>satisfied</u> (in IPER Sec. V all 3 boxes <u>must</u> be YES for <u>all</u> claims), -- | add \$100/\$50    | +0 | 962/963 |

27. **SUBTOTAL = \$1262**

28. If Assignment box 19 above is X'd, add Assignment Recording fee of ---\$40 +0 (581)

29. If box 15a is X'd, determine whether inventorship on Declaration is different than in international stage. If yes, add (per Rule 497(d)) ---\$130 +0 (098)

30. Attached is a check to cover the ----- **TOTAL FEES \$1262**

Our Deposit Account No. 03-3975

Our Order No. 18679 | 290642

CR# M#



00909

**CHARGE STATEMENT:** The Commissioner is hereby authorized to charge any fee specifically authorized hereafter, or any missing or insufficient fee(s) filed, or asserted to be filed, or which should have been filed herewith or concerning any paper filed hereafter, and which may be required under Rules 16-18 and 492 (missing or insufficient fee only) now or hereafter relative to this application and the resulting Official document under Rule 20, or credit any overpayment, to our Account/Order Nos. shown above for which purpose a duplicate copy of this sheet is attached.

This CHARGE STATEMENT does not authorize charge of the issue fee until/unless an issue fee transmittal form is filed

**Pillsbury Winthrop LLP  
Intellectual Property Group**

By Atty: Richard A. Steinberg

Reg. No. **26,588**

Sig: Richard A. Steinberg

Fax: (703) 905-2500

Tel: (703) 905-2039

Atty/Sec: RAS/cdw

NOTE: File in duplicate with 2 postcard receipts (PAT-103) & attachments.

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re PATENT APPLICATION of:

WOODHOUSE et al.

Group Art Unit: TBA

Application No.: TBA

Examiner: TBA

Filed: January 23, 2002

FOR: CLEANING COMPOSITIONS

\* \* \* \* \*

January 23, 2002

PRELIMINARY AMENDMENTHon. Commissioner of Patents  
Washington, D.C. 20231

Sir:

Prior to examination on the merits, please amend the above-identified patent in the manner set forth below.

IN THE SPECIFICATION:

At the top of the first page, just under the title, insert

--This application is the National Phase of International Application PCT/GB00/02785 filed July 24, 2000, which designated the U.S. and that International Application was published under PCT Article 21(2) in English. The PCT application is hereby incorporated in its entirety by reference. --

## IN THE CLAIMS:

Please amend the claims as follows:

2. (Amended) A cleaning composition according to claim 1, in which the water-swellaible agent comprises, in its anhydrous state, no more than 15% of the combined weight of said

**WOODHOUSE – Filed January 23, 2002**

inorganic material and said agent of the granular disintegrant.

3. (Amended) A cleaning composition according to claim 1, in which the water-swellaable agent comprises, in it's anhydrous state, no more than 10% of the combined weight of said inorganic material and said agent of the granular disintegrant.

4. (Amended) A cleaning composition according to claim 1, in which the water-swellaable agent comprises, in it's anhydrous state, no more than 8% of the combined weight of said inorganic material and said agent of the granular disintegrant.

5. (Amended) A cleaning composition according to claim 1, in which the water-swellaable agent comprises, in it's anhydrous state, at least 1% of the combined weight of said inorganic material and said agent of the granular disintegrant.

6. (Amended) A cleaning composition as claimed in claim 1 in which the inorganic material comprises a silica.

7. (Amended) A cleaning composition as claimed in claim 1 in which the inorganic material acts as functional ingredient of the cleaning composition.

8. (Amended) A cleaning composition as claimed in claim 1 in which the inorganic material comprises an aluminosilicate.

11. (Amended) A cleaning composition as claimed in claim 1 in which the organic material comprises from about 10% to about 60% by weight of the cleaning composition.

13. (Amended) A cleaning composition as claimed in claim 1 in which the water-swellaable agent has an average primary particle size of no more than 200  $\mu\text{m}$ .

**WOODHOUSE – Filed January 23, 2002**

14. (Amended) A cleaning composition as claimed in claim 1 in which the water-swelling agent has a water swelling capacity of at least 5 ml/gram.

15. (Amended) A cleaning composition as claimed in claim 1 in which the water-swelling agent is selected from the group consisting of cellulose, cross-linked cellulose, carboxymethyl cellulose, pre-gelatinised starch, cross-linked starch and cross-linked polyvinyl pyrrolidone.

16. (Amended) A cleaning composition as claimed in claim 1 in which the moulded body consists entirely of said cleaning composition.

17. (Amended) A cleaning composition as claimed in claim 1 in which only part of the moulded body is constituted by said cleaning composition, the remainder of the moulded body being constituted by at least one other ingredient for use in detergent and cleaning applications such as fabric washing, dishware washing, stain removal and water softening.

18. (Amended) A cleaning composition as claimed in claim 1 in which the amount of water-swelling agent is less than 2% by weight of the cleaning composition.

19. (Amended) A cleaning composition as claimed in claim 1 in which the granular disintegrant is present in an amount in the range 1 to 25% by weight of the total cleaning composition.

WOODHOUSE – Filed January 23, 2002

REMARKS

After introduction of the amendment set forth above, claims 1-22 will be pending in the application of which claims 1, 21 and 22 are independent. Claim 2-8, 11 and 13-19 have been amended to add the appropriate dependencies or to eliminate multiple dependency of the claims. Support for the above amendments can be found throughout the original application as filed. Applicants submit that no new matter has been introduced by the amendment.

Respectfully submitted,

PILLSBURY WINTHROP, LLP

By: Richard A. Steinberg  
Richard A. Steinberg  
Reg. No. 26,588  
Paul L. Sharer  
Reg. No. 36,004  
Tel. No.: (703) 905-2039  
Fax No.: (703) 905-2500

PLS/RAS:cdw  
1600 Tysons Boulevard  
McLean, VA 22102  
(703) 905-2000

Enclosure: Appendix

WOODHOUSE – Filed January 23, 2002

APPENDIX

VERSION WITH MARKINGS SHOWING CHANGES MADE

IN THE CLAIMS:

The claims are amended as follows:

2. (Amended) A cleaning composition according to claim 1, in which the water-swellaable agent comprises, in it's anhydrous state, no more than 15% of the combined weight of said inorganic material and said agent of the granular disintegrant.
3. (Amended) A cleaning composition according to claim 1, in which the water-swellaable agent comprises, in it's anhydrous state, no more than 10% of the combined weight of said inorganic material and said agent of the granular disintegrant.
4. (Amended) A cleaning composition according to claim 1, in which the water-swellaable agent comprises, in it's anhydrous state, no more than 8% of the combined weight of said inorganic material and said agent of the granular disintegrant.
5. (Amended) A cleaning composition according to claim 1, in which the water-swellaable agent comprises, in it's anhydrous state, at least 1% of the combined weight of said inorganic material and said agent of the granular disintegrant.
6. (Amended) A cleaning composition as claimed in [any one of the preceding claims] claim 1 in which the inorganic material comprises a silica.



**WOODHOUSE – Filed January 23, 2002**

7. (Amended) A cleaning composition as claimed in [any one of the preceding claims] claim 1 in which the inorganic material acts as functional ingredients of the cleaning composition.

8. (Amended) A cleaning composition as claimed in [any one of the preceding claims] claim 1 in which the inorganic material comprises an aluminosilicate.

11. (Amended) A cleaning composition as claimed in [any one of Claims 7 to 10] claim 1 in which the organic material comprises from about 10% to about 60% by weight of the cleaning composition.

13. (Amended) A cleaning composition as claimed in [any one of the preceding claims] claim 1 in which the water-swellaable agent has an average primary particle size of no more than 200  $\mu\text{m}$ .

14. (Amended) A cleaning composition as claimed in [any one of the preceding claims] claim 1 in which the water-swellaable agent has a water swelling capacity of at least 5 ml/gram.

15. (Amended) A cleaning composition as claimed in [any one of the preceding claims] claim 1 in which the water-swellaable agent is selected from the group consisting of cellulose, cross-linked cellulose, carboxymethyl cellulose, pre-gelatinised starch, cross-linked starch and cross-linked polyvinyl pyrrolidone.

16. (Amended) A cleaning composition as claimed in [any one of the preceding claims] claim 1 in which the moulded body consists entirely of said cleaning composition.

17. (Amended) A cleaning composition as claimed in [any one of Claims 1 to 15] claim 1 in which only part of the moulded body is constituted by said cleaning composition, the remainder of the moulded body being constituted by at least one other ingredient for use in detergent and cleaning applications such as fabric washing, dishware washing, stain removal and water softening.

18. (Amended) A cleaning composition as claimed in [any one of the preceding

**WOODHOUSE – Filed January 23, 2002**

claims] claim 1 in which the amount of water-swellable agent is less than 2% by weight of the cleaning composition.

19. (Amended) A cleaning composition as claimed in [any one of the preceding claims] claim 1 in which the granular disintegrant is present in an amount in the range 1 to 25% by weight of the total cleaning composition.

### CLEANING COMPOSITIONS

This invention relates to cleaning compositions and, in particular, particulate cleaning compositions to be formed into moulded bodies for use in, for example, fabric washing, dishware washing, stain removal and water softening.

5 Detergent compositions in the form of tablets are widely described and are currently enjoying increasing popularity with consumers. They are described, for example, in GB 0 911 204 (Unilever), US 3 953 350 (Kao), DE 19 637 606 (Henkel), EP 0 711 827 (Unilever) and WO 98/40463 (Henkel). Tablets for machine dishwashing applications are described in, for example, WO 96/28530 (P&G). Tabletting detergents and cleaning  
10 compositions have several advantages over powdered or liquid compositions: they are easier to dispense and handle, do not require measuring to obtain the correct dose and, being compact, are more economical to store and transport.

Tablets of cleaning compositions are generally made by compression or compaction of a quantity of the composition in the form of particles. Production of tablets which are  
15 sufficiently hard and strong to withstand storage and handling requires a relatively high pressure to be used in this compaction process. It is then necessary that, despite this compaction, the tablets are able to disperse and dissolve rapidly when added to wash water.

One approach to achieving good dispersion of the tablet is to include in the tablet a particulate insoluble but water-swellaable agent. These particles then swell with ingress of water, leading to stresses in the tablet and thence to break-up of the tablet. Thus WO 98/55583 (Unilever) describes the use of 'water-insoluble, water-swellaable polymeric material' which 'promotes disintegration of the tablets in water'. Typical swelling agents which have been disclosed as possible tablet disintegrating agents are starches, cellulose and cellulose derivatives, alginates, dextrans, cross-linked polyvinyl pyrrolidones, gelatines and formaldehyde casein as well as a wide variety of clay minerals and certain ion-exchange resins.  
25

These swelling agents have no function in fabric washing except to aid tablet disintegration. Furthermore, because they are insoluble and of relatively large particle size, they tend to deposit on clothes during the wash (see, for example, WO 98/55575 (Henkel) and WO 98/55582). As a result, several attempts have been made to minimise the deposition of these  
30 disintegrants, for example by combining such a water-swellaable, insoluble disintegrant with a second, highly soluble disintegrating aid – see WO 98/55582 (Unilever). Other attempts have included use of a preferred particle size of the disintegrant. Thus, for example, WO 98/55583 (Unilever) claims use of such material at a particle dimension of at least 400  $\mu\text{m}$  to give more efficient disintegration. On the other hand, WO 98/55575 (Henkel) teaches the use of cellulose  
35 disintegrating aids with a particle size of less than 100  $\mu\text{m}$ , in order to minimise deposition. This material is co-granulated with 'microcrystalline cellulose and/or one or several ingredients of detergents and cleaning agents'.

Surprisingly, we have now found that if a water-swella-  
ble disintegrating aid is co-granulated with an insoluble or sparingly soluble, hydrophilic solid before being incorporated  
into a tablet, then the disintegrant is much more efficient in disintegrating the tablet in use. Thus,  
less of the disintegrating aid needs to be added for effective disintegration, lowering the  
probability of deposition of the disintegrating aid on the substrate being cleaned.

The present invention seeks to provide a particulate cleaning composition in the form  
of a moulded body and which is relatively inexpensive to manufacture and sufficiently robust to  
withstand handling during production and packaging processes but readily breaks up and  
dissolves when contacted with an aqueous medium during the cleaning process for which it is  
intended without resulting in undue deposition on the substrate being cleaned.

According to the present invention there is provided a cleaning composition, the  
composition including disintegrant in the form of granules comprising a water insoluble inorganic  
material and a water-swella-ble agent which, in its anhydrous state, comprises no more than  
20% of the combined weight of said inorganic material and said agent of the granular  
disintegrant, the granules being combined with the active ingredients of the cleaning  
composition in a compacted moulded body.

According to a particular aspect of the invention, a granular composition suitable for  
use in a cleaning composition consists essentially of a water insoluble inorganic material and a  
water-swella-ble agent which, in its anhydrous state, comprises no more than 20% of the  
combined weight of said inorganic material and said agent of the granular composition.

By "water insoluble", we mean a compound with a water solubility of less than 5  
grams, preferably less than 1 gram, per 100 grams water (at a temperature of 25°C).

Preferably, the water-swella-ble agent comprises, in its anhydrous state, no more than  
15%, more preferably no more than 10%, of the combined weight of said inorganic material and  
said agent of the granular disintegrant. In a typical composition of the invention, the water-  
swella-ble agent comprises, in its anhydrous state, no more than 8%, e.g. 7.5% or less, of the  
combined weight of said inorganic material and said agent. Generally, at least 1% of the  
combined weight of the water-swella-ble agent and the inorganic material in the granules  
comprises water-swella-ble agent.

A feature of the invention is the relatively small amount of water-swella-ble agent that  
may be employed while securing satisfactory properties for the compacted cleaning  
composition. Frequently, the amount of water-swella-ble agent in the cleaning composition is  
less than 2% by weight. Preferably, the amount is less than 1% of the cleaning composition but,  
usually, at least 0.2% of the water-swella-ble agent is present in the cleaning composition.

In one embodiment of the invention the inorganic material used in the formation of  
the disintegrant granules comprises a silica.

In a second embodiment of the invention the inorganic material used in the formation of the disintegrant granules conveniently comprises a material which acts as a functional ingredient of the cleaning composition. In this instance, the inorganic material may be an aluminosilicate such as zeolite P, A or X or mixtures thereof, with zeolite P being preferred.

5 Alkali metal aluminosilicates, especially zeolites, are commonly used in detergent compositions as a detergency builder. Where a cleaning composition of the invention is one containing an alkali metal aluminosilicate as detergency builder, preferably at least part of the aluminosilicate constituent of the cleaning composition is employed as the inorganic material used in the formation of the disintegrant granules. For instance, the aluminosilicate constituent typically comprises about 10 to about 60% by weight of the cleaning composition and  
10 preferably, when zeolite is used in the disintegrant granules and as a detergency builder, then at least 1% of the detergent composition comprises a zeolite constituent employed in the form of disintegrant granules.

The water-swellaable agent preferably has an average primary particle size up to  
15 about 600  $\mu\text{m}$ , but, conveniently, has an average primary particle size of no more than 200  $\mu\text{m}$ , preferably no more than 100  $\mu\text{m}$ , and a water swelling capacity of at least 5 ml/gram, preferably 10 ml/gram and more preferably 20 ml/gram as determined in the test described hereinafter.

Typically the water-swellaable agent comprises polymer, frequently a wholly or partially cross-linked polymer, e.g. natural cellulose, cross-linked cellulose, (sodium) carboxymethyl cellulose, cross-linked sodium carboxymethyl cellulose, pre-gelatinised starch, cross  
20 linked starch, or cross linked polyvinyl pyrrolidone. Currently preferred are Aquasorb A500 (ex Hercules) and Ac-Di-Sol (ex FMC Corp).

The moulded body formed using the cleaning composition of the present invention may consist wholly of the cleaning composition or alternatively the moulded body may comprise  
25 a number of discrete portions, at least one of which comprises a cleaning composition in accordance with the invention. In this event, the remaining portion or portions of the moulded body may be constituted by at least one other ingredient, usually one suitable for use in detergent and cleaning applications such as fabric washing, dishware washing, stain removal and water softening.

Cleaning compositions of the invention may also contain, as essential ingredients, one or more detergency builders (wholly or partly incorporated in the disintegrant granules), and/or one or more detergent-active compounds which may be chosen from soap and non-soap anionic, cationic, nonionic, amphoteric and zwitterionic detergent-active compounds, and mixtures thereof and/or other conventional additives.

35 A further aspect of the invention comprises a process for the preparation of a cleaning composition comprising forming a granular disintegrant composition consisting essentially of a water insoluble inorganic material and a water-swellaable agent which, in its

anhydrous state, comprises no more than 20% of the combined weight of said inorganic material and said agent of the granular composition and mixing said granular composition with one or more detergent-active compounds and, optionally, with one or more detergency builders.

Alkali metal aluminosilicates are favoured as environmentally acceptable water-insoluble builders, e.g. zeolites A, X and P or mixtures thereof. Other inorganic detergency builders include layered sodium silicate as described in US-A-4 664 839 and marketed by Hoechst as SKS-6, and alkali metal (generally sodium) carbonate. Water-soluble phosphorous containing detergency building compounds such as alkali metal orthophosphates, metaphosphates, pyrophosphates and polyphosphates may be used. Also possible are organic detergency builders such as polycarboxylate polymers, e.g. polyacrylates, acrylic/maleic polymers, and acrylic phosphonates, monomeric polycarboxylates, e.g., gluconates, oxydisuccinates, glycerol mono- di- and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates and hydroxyethyliminodiacetates.

Many suitable detergent-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

The preferred detergent-active compounds that can be used are soaps and synthetic non-soap anionic and nonionic compounds. Anionic surfactants are well known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly sodium linear alkylbenzene sulphonates having an alkyl chain length of  $C_8 - C_{15}$ ; primary and secondary alkyl sulphates, particularly sodium  $C_8 - C_{15}$  primary alcohol sulphates; olefin sulphonates; alkane sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates.

Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, and ethoxylates of esterified fatty acids, especially the  $C_8 - C_{15}$  primary and secondary alcohols ethoxylated with an average of from 3 to 20 moles of ethylene oxide per mole of alcohol.

The choice of surfactant, and the amount present, will depend on the intended use of the detergent composition. For example, for machine dishwashing a relatively low level of a low-foaming nonionic surfactant is generally preferred. In fabric washing compositions, different surfactant systems may be chosen, as is well known by the skilled detergent formulator, for handwashing products and for machine washing products.

The total amount of surfactant present will of course depend on the intended end use and may be as low as 0.5% by weight of the total composition, for example, in a machine dishwashing composition, or as high as 60% by weight of the total composition, for example, in a composition for washing fabrics by hand. For fabric washing compositions in general, an amount of from 5 to 40% by weight of the total composition is generally appropriate.

Generally, cleaning compositions of the invention will contain from 1 to 20% by weight of the disintegrant granules based on total weight of the composition. Frequently the cleaning compositions will contain from 4 to 10 % by weight of the disintegrant granules.

A suitable type of cleaning composition suitable for use in most automatic fabric washing machines contains both anionic and nonionic surfactants. Cleaning compositions according to the invention may also suitably contain a bleach system. Machine dishwashing compositions may suitably contain a chlorine bleach, while fabric washing compositions may contain peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, which may be employed in conjunction with activators to improve bleaching action at low wash temperatures. Again, the skilled detergent worker will have no difficulty in applying the normal principles to choose a suitable bleach system.

Other materials that may be present in detergent compositions of the invention include sodium silicate, fluorescers, antiredeposition agents, inorganic salts such as sodium sulphate, enzymes, lather control agents or lather boosters as appropriate, pigments, and perfumes. This list is not intended to be exhaustive.

## **Procedures and Tests**

### **Granule Production**

The granules of inorganic material and swelling agent may be prepared by any of the methods that will be known to those skilled in the art, e.g. by blending the dry ingredients in a mixer (such as a Pek mixer available from George Tweedy & Co of Preston - 28lb S.A. Machine) and compacting on a roller compactor (Alexanderwerk WP50 - manufactured by Alexanderwerk AG, D 5630 Remscheid 1, Germany). A typical preparative method is now described in detail with reference to silica as the inorganic material. Silica and water swelling organic particulate are blended together, in the appropriate proportions, in a Pek mixer for 30 minutes. A minimum of 2 kg of blended material so prepared is compacted by feeding into an Alexanderwerk roller compactor, fitted with a sintered block vacuum deaeration system. The roller pressure setting is selected according to the strength of granule desired, higher pressures leading to stronger granules. Generally, roller pressure is between 8 and 25 MPa and a typical roller pressure is 10 MPa. The compacted material from the compactor is fed into a granulator, which forms part of the machine, and forced through a mesh and the resulting granules are then screened to the desired particle size range, e.g. an average particle size of 250 to 1500  $\mu\text{m}$ , using standard laboratory sieves. Preferably, the particles have a size range of 500 to 1200  $\mu\text{m}$ .

### **Tablet Production**

Tablets used in the Examples that follow were produced using a 45 mm diameter die set (stainless steel) in conjunction with a Universal Testing Machine Type No. Z030 from Zwick GmbH, Ulm, Germany. A known quantity, 40-45 grams, of the cleaning composition which

metal cage 20 cm in diameter with 1 cm<sup>2</sup> perforations. The cage was lowered into the 5 litre vessel and left for 60 seconds. The cage was then removed from the water, residue of the tablets was placed on an aluminium tray, dried for 24 hrs at 105° C and weighed to determine the percentage which had not disintegrated.

#### 5 Determination of Tablet Conductivity Profile

The tablet conductivity profile provides an indication of the extent to which various tablets (e.g. different compositions, different densities) dissolve under the defined conditions. Conductivity measurements were obtained from the conductivity probe mentioned in Method 1 above at the same time as the tablet disintegration was measured.

10 Measurements of conductivity and pH were taken, initially at 30 second intervals for ten minutes and thereafter at one minute intervals for a further 20 minutes or until the conductivity measurements were observed to have reached a plateau corresponding to substantially total dissolution of the soluble portion of the tablet, i.e. equilibration of the tablet with water. This procedure was repeated for a number of tablets having different compositions  
15 and different densities.

#### Determination of water swelling capacity of water-swellaable agent

To demonstrate the water swelling capacity of the water-swellaable agent, 19.6 g of the agent was blended with 0.4 g of ultramarine pigment and compressed into a tablet using a laboratory tablet press at about 250 Mpa to give a tablet 32 mm in diameter. This was crushed  
20 and sieved to give granules 500-1000 µm in size. A glass tube, 33 mm in internal diameter and about 30 cm long with a sintered porous glass disc (porosity 1) fitted at one end was immersed upright, with said one end lowermost, in a large beaker of water (at 25° C) so that the water level rose to about 14 cm above the sintered glass. 1 g of granules was added to the tube and allowed to settle onto the sintered glass disc. With this arrangement water has access to the  
25 granules from both above and below. The granules immediately began to swell, forming a jelly-like mass. The ultramarine pigment imparted a blue colour to the mass making it easy to see the top and to record its height. The height of the swelling mass was recorded at intervals and showed an initial rapid rise followed by a levelling off after about 20-30 minutes. From the diameter of the tube, the volume of the swollen mass can be calculated. The result was  
30 expressed as ml/g water-swellaable agent after 20 minutes.

#### EXAMPLE 1

Conductivity and disintegration profiles were investigated for a number of tablet formulations and densities, all based on concentrated Persil (Registered Trade Mark) original  
35 non-Biological detergent powder as manufactured by Lever Brothers of Kingston-upon-Thames, UK - formulation as sold in the UK. The detergent powder was blended with different amounts of disintegrant granules. In each instance, the disintegrant granules comprised a water



comprised the compositions mentioned in the Examples below was placed in the die, the die plunger was inserted and the assembly was placed between the platens of the Zwick machine which was operated to apply a predetermined pressure to produce a tablet having a defined density and, in particular, a dimensionally stable and fracture resistant tablet. Tablets thus produced were cylindrical in shape, with a diameter of 45 mm and a height of about 20 mm. Tablets with different densities were produced in order to determine the tablet disintegration and conductivity profiles. Tablets prepared had densities in the range 1250-1450 kg/m<sup>3</sup>, which are typical values for commercial fabric washing tablets found in the Western European market in 1998-9.

#### Determination of tablet disintegration profile

##### Method 1 (Dynamic)

The tablet disintegration profile provides an indication of the extent to which various tablets (e.g. different compositions, different densities) disintegrate under the defined conditions.

4500 g of demineralised water at 20°C were added to a 5 litre vessel fitted with pH, conductivity and temperature probes and maintained at a constant temperature of 20°C by immersion in a water bath. The tablets to be tested were inserted into a metal cage having the dimensions 9 cm x 4.7 cm x 2.7 cm and having 16 apertures (each about 2 mm square) per cm<sup>2</sup>. The metal cage was attached to the shaft of an overhead stirrer (Heidolph/Janke and Kunkel stirrer) to allow it and its contents to be rotated while immersed in the demineralised water. Prior to testing, the empty cage was immersed in the demineralised water and rotated at 80 rpm for a short period of time until the temperature of the demineralised water as detected by the temperature probe had stabilised at 20 ± 0.2°C. At this time, the conductivity, pH and temperature values registered by the respective probes were recorded. The stirrer was then switched off to allow the cage to be raised out of the water so that a pre-weighed detergent tablet to be investigated could be inserted into the cage. The cage was then re-immersed in the demineralised water together with the inserted tablet and the stirrer was switched on to resume rotation of the container at 80 rpm. Measurements of conductivity and pH, initially at 15 second intervals for one minute and thereafter at one minute intervals, were made over a period of 10 minutes after which time the cage was raised out of the demineralised water to allow the residue of the tablet to be removed. The residue was then dried in an oven at 105°C so that the dry weight of the residue could be calculated as a percentage of the original tablet weight. This procedure was repeated for a number of tablets having different compositions and different densities.

##### Method 2 (Static)

4500g of tap water at 20° C were added to a 5 litre vessel, which was maintained at 20° C by immersion in a water bath. The tablets to be tested were weighed and inserted into a

insoluble inorganic material, specifically a zeolite or a silica or a combination thereof, and a water-swellaable agent. For comparative purposes, granules consisting of Persil powder alone or comprising a water-swellaable agent or a mixture of a water soluble material, specifically sodium silicate or sodium carbonate, and a water-swellaable material were also prepared and tested. In the Examples given below, Doucil A24 (Trade Mark) is a P-type zeolite sold by Crosfield Limited of Warrington, UK; SD2255 is a silica<sup>\*</sup> also obtainable from Crosfield Limited; Doucil 4A (Trade Mark) is a 4A zeolite obtainable from Crosfield Limited; the sodium disilicate is obtainable from Crosfield Limited under the trade mark Pyramid 95; the sodium carbonate is obtainable from Solvay Chemicals Limited (identified in their product literature as Soda Ash (Sodium Carbonate) Light Rheinberg); and the water-swellaable agent was sodium carboxymethylcellulose as sold under the trade mark Aquasorb A500 by Hercules Limited of Salford, UK.

TABLE 1

| Property                         | SD2255 | Doucil A24 | Doucil 4A | Sodium Disilicate | Soda Ash  | Aquasorb |
|----------------------------------|--------|------------|-----------|-------------------|-----------|----------|
| Surface Area (m <sup>2</sup> /g) | 650    | NM         | NM        | NM                | NM        | NM       |
| Pore Volume (ml/g)               | 1.3    | NM         | NM        | NM                | NM        | NM       |
| APS (µm)                         | 5      | 1.2*       | 3*        | 100*              | See below | 40*      |
| Moisture Content (% by weight)   | 2      | 10*        | 20*       | 18-20*            | < 1.5     | 5*       |
| Oil absorption (g/100g)          | 228    | 60*        | 40*       | NM                | NM        | NM       |

NM = Not measured

In Table 1, APS represents average particle size ( $d_{50}$ ) as measured using a Malvern Mastersizer (Trade Mark) obtainable from Malvern Instruments in the UK and the values marked \* are taken from typical data for the product or from specifications supplied by the manufacturer. The Soda Ash used in the Examples had a bulk density of 0.53 kg/dm<sup>3</sup> and was found to have a particle size distribution (by sieve analysis) as follows:

- > 1000 µm = 1wt %
- 500 - 1000 µm = 0.5 wt %
- 250 - 500 µm = 3.5 wt %
- 75 - 250 µm = 74.5wt %
- 0 - 75 µm = 20.5wt %

The different formulations of the disintegrant granules (on a by weight basis) are given in Table 2.

TABLE 2

| Granule Code | Wt. % of Aquasorb A500 in granule | Remainder of Granule (Wt. % and Material) |
|--------------|-----------------------------------|---|
| A            | 10                                | 90% SD2255 Silica                         |
| B            | 10                                | 45% SD2255 Silica,<br>45% Doucil A24      |
| C            | 10                                | 90% Doucil 4A                             |
| D            | 10                                | 90% Doucil A24                            |
| E            | 7.5                               | 92.5% Doucil A24                          |
| F            | 5                                 | 95% Doucil A24                            |
| G            | 10                                | Pyramid 95                                |
| H            | 10                                | Sodium Carbonate                          |

5 The granules coded G and H contain inorganic materials which are water soluble and as such are not within the scope of the present invention. These particular Examples are included for comparative purposes.

10 A series of tablets were prepared at a standard density of  $1325 \pm 10 \text{ kg/m}^3$ . Tablets 1A to 1H contain 2% by weight of granules A to H respectively, the other 98% being formed from concentrated Persil original non-Biological detergent powder. Tablet 1J was fabricated entirely from the same Persil powder. Tablets 1K and 1L were prepared from the same Persil powder, but incorporated 0.2% and 2% by weight of Aquasorb A500 powder respectively.

15 Table 3 shows the level of disintegration and the conductivity obtained after 10 minutes immersion in water for these tablets using the experimental protocol described above in Method 1. The conductivity measurements are representative of the degree of dissolution of the soluble ionic constituents of the Persil detergent powder, the higher the conductivity value the greater the degree of tablet dissolution. The measurement of disintegration shows the level of undisintegrated residue retained in the 'cage'. Thus a high value indicates a poorly disintegrating tablet.

TABLE 3

| Tablet Code | Conductivity (microSiemen) | Undisintegrated Residue (%) |
|-------------|----------------------------|-----------------------------|
| 1A          | 3800                       | 5                           |
| 1B          | 4100                       | 0                           |
| 1C          | 4000                       | 0                           |
| 1D          | 3970                       | 0                           |
| 1E          | 3700                       | 2                           |
| 1F          | 3520                       | 10                          |
| 1G          | 1060                       | 84                          |
| 1H          | 2840                       | 29                          |
| 1J          | 1720                       | 49                          |
| 1K          | 1800                       | 48                          |
| 1L          | 630                        | 80                          |

The data clearly demonstrate the following:

- 1) The Tablet 1J, composed entirely of concentrated Persil powder, does not disintegrate or dissolve well; after 10 minutes it is only about 50% disintegrated.
- 2) Addition of 0.2% Aquasorb A500 (Tablet 1K) has no appreciable effect (this is equivalent to the amount of Aquasorb added via granule incorporation in Tablets 1A to 1D, 1G and 1H).
- 3) Addition of more Aquasorb in Tablet 1L (equivalent to the total weight addition of granules in Tablets 1A-1H) appears to suppress disintegration and dissolution.
- 4) Tablets 1A-1D are essentially fully disintegrated/dissolved after 10 minutes.
- 5) In contrast, when the Aquasorb has been co-granulated with a soluble material (Tablets 1G, 1H), the disintegration and dissolution is far less effective. In the case of silicate, the granules actually appear to retard disintegration relative to Tablet 1J.
- 6) Even when the level of Aquasorb in the granules is reduced to 7.5% or 5% (Tablets 1E, 1F, respectively) disintegration of the tablets is very well advanced after 10 minutes.

## EXAMPLE 2

Table 4 below shows data for Tablets 2E, 2F equivalent to the data in Table 3. These tablets which are similar to the tablets used in Example 1 but contain granules E and F respectively, incorporated into tablets at 4% by weight instead of 2%. The test method for measuring disintegration was Method 1. Again, it is clear that, by increasing the weight of granule in the tablet at these lower levels of Aquasorb inclusion, the excellent disintegrating properties of the granules can be retained without the need to significantly increase the total weight of disintegrating polymer in the tablet (since 4% inclusion of granule F corresponds to 2% of granule D in terms of the total weight of Aquasorb introduced into the granule).

TABLE 4

| Tablet Code | Conductivity (microSiemen) | Undisintegrated Residue (%) |
|-------------|----------------------------|-----------------------------|
| 2E          | 3950                       | 0                           |
| 2F          | 3900                       | 0                           |

## EXAMPLE 3

Table 5 below shows further data for disintegration/conductivity (using disintegration Method 1) for tablets containing various of the granules, again incorporated into the tablets at 2% by weight. These tablets are identified as 3X, where the X is the letter corresponding to the granule identity in Table 2. In this case, the tablets have been prepared at a higher density ( $1350 \pm 10 \text{ kg/m}^3$ ). At this higher density, it is possible to discriminate between the performance of the different granules A to D. From this data, it appears that the zeolite-containing granules are preferred over the silica-containing variant, with the granules prepared from Doucil A24 being the best performing disintegrating agents.

TABLE 5

| Tablet Code | Conductivity (microSiemen) | Undisintegrated Residue (%) |
|-------------|----------------------------|-----------------------------|
| 3A          | 3060                       | 21                          |
| 3B          | 3500                       | 9                           |
| 3C          | 3060                       | 13                          |
| 3D          | 3860                       | 9                           |

## EXAMPLE 4

A number of tablets were prepared using a standard detergent base powder, similar to concentrated Persil powder, but without minor additives, such as perfume. Tablets containing disintegrant granules as shown in Table 6 below were prepared at a nominal density of  $1250 \text{ kg/m}^3$  with 5% by weight of granules in the final detergent composition. The disintegrant granules used were all based on the zeolite P, Doucil A24, which consisted of 90% aluminosilicate and 10% water by weight.

TABLE 6

| Granule Code | Water-swellable agent in granule (% by weight) |
|--------------|--|
| 4M           | Aquasorb A500 (7.5)                            |
| 4N           | Ac-Di-Sol <sup>1</sup> (5.0)                   |
| 4O           | Ac-Di-Sol <sup>1</sup> (7.5)                   |
| 4P           | Ac-Di-Sol <sup>1</sup> (10.0)                  |
| 4Q           | Ac-Di-Sol <sup>1</sup> (15.0)                  |
| 4R           | Cellulose powder BFT <sup>2</sup> Fines (7.5)  |
| 4S           | National 78- 1551 <sup>3</sup> (7.5)           |
| 4T           | Arbocel FT40 <sup>4</sup> (7.5)                |

<sup>1</sup>Ac-Di-Sol is a croscarmellulose sodium available from FMC Corporation, Philadelphia USA.

<sup>2</sup>Cellulose powder BFT is a granulated sulphite cellulose available from Vendico Chemical AB, Malmö, Sweden.

<sup>3</sup>National 78-1551 is a pre-gelatinised starch available from National Starch & Chemical, Manchester, UK.

<sup>4</sup>Arbocel FT40 is a fibrous natural cellulose available from J. Rettenmaier & Söhne, Rosenberg, Germany.

The disintegration of the tablets was measured using Method 2, described hereinbefore, and the results are given in Table 7 below.

TABLE 7

| Disintegrant code | Undisintegrated residue (%w/w) |
|-------------------|--------------------------------|
| 4M                | 40                             |
| 4N                | 42                             |
| 4O                | 32                             |
| 4P                | 36                             |
| 4Q                | 34                             |
| 4R                | 33                             |
| 4S                | 32                             |
| 4T                | 43                             |
| no disintegrant   | 87                             |

In general, the amount of residue found using Method 2 is larger than that found using Method 1, but the results still clearly demonstrate that the tablets containing disintegrant granules disintegrate to a much larger extent than tablets containing no granules.

**CLAIMS**

1. A cleaning composition, the composition including disintegrant in the form of granules comprising a water insoluble inorganic material and a water-swellaable agent which, in its anhydrous state, comprises no more than 20% of the combined weight of said inorganic material and said agent of the granular disintegrant, the granules being combined with the active ingredients of the cleaning composition in a compacted moulded body.
2. A cleaning composition in which the water-swellaable agent comprises, in its anhydrous state, no more than 15% of the combined weight of said inorganic material and said agent of the granular disintegrant.
3. A cleaning composition in which the water-swellaable agent comprises, in its anhydrous state, no more than 10% of the combined weight of said inorganic material and said agent of the granular disintegrant.
4. A cleaning composition in which the water-swellaable agent comprises, in its anhydrous state, no more than 8% of the combined weight of said inorganic material and said agent of the granular disintegrant.
5. A cleaning composition in which the water-swellaable agent comprises, in its anhydrous state, at least 1% of the combined weight of said inorganic material and said agent of the granular disintegrant.
6. A cleaning composition as claimed in any one of the preceding claims in which the inorganic material comprises a silica.
7. A cleaning composition as claimed in any one of the preceding claims in which the inorganic material acts as functional ingredient of the cleaning composition.
8. A cleaning composition as claimed in any one of the preceding claims in which the inorganic material comprises an aluminosilicate.
9. A cleaning composition as claimed in Claim 8 in which the inorganic material comprises a zeolite.
10. A cleaning composition as claimed in Claim 9 in which the inorganic material comprises a zeolite P.
11. A cleaning composition as claimed in any one of Claims 7 to 10 in which the inorganic material comprises from about 10% to about 60% by weight of the cleaning composition.
12. A cleaning composition as claimed in Claim 11 in which the cleaning composition contains at least 1% by weight of the inorganic material embodied in the form of disintegrant granules.
13. A cleaning composition as claimed in any of the preceding claims in which the water-swellaable agent has an average primary particle size of no more than 200  $\mu\text{m}$ .

14. A cleaning composition as claimed in any one of the preceding claims in which the water-swellaible agent has a water swelling capacity of at least 5 ml/gram.
15. A cleaning composition as claimed in any one of the preceding claims in which the water-swellaible agent is selected from the group consisting of cellulose, cross-linked cellulose, carboxymethyl cellulose, sodium carboxymethyl cellulose, cross-linked sodium carboxymethyl cellulose, pre-gelatinised starch, cross-linked starch and cross-linked polyvinyl pyrrolidone.
16. A cleaning composition as claimed in any one of the preceding claims in which the moulded body consists entirely of said cleaning composition.
17. A cleaning composition as claimed in any one of Claims 1 to 15 in which only part of the moulded body is constituted by said cleaning composition, the remainder of the moulded body being constituted by at least one other ingredient for use in detergent and cleaning applications such as fabric washing, dishware washing, stain removal and water softening.
18. A cleaning composition as claimed in any one of the preceding claims in which the amount of water-swellaible agent is less than 2% by weight of the cleaning composition.
19. A cleaning composition as claimed in any one of the preceding claims in which the granular disintegrant is present in an amount in the range 1 to 20% by weight of the total cleaning composition.
20. A granular composition suitable for use in a cleaning composition consisting essentially of a water insoluble inorganic material and a water-swellaible agent which, in its anhydrous state, comprises no more than 20% of the combined weight of said inorganic material and said agent of the granular composition.
21. A process for the preparation of a cleaning composition comprising forming a granular disintegrant composition consisting essentially of a water insoluble inorganic material and a water-swellaible agent which, in its anhydrous state, comprises no more than 20% of the combined weight of said inorganic material and said agent of the granular composition and mixing said granular composition with one or more detergent-active compounds and, optionally, with one or more detergency builders.
22. A process as claimed in claim 21 in which the detergent-active compound is a soap, a synthetic non-soap anionic compound or a synthetic non-soap nonionic compound.



**ABSTRACT**

A cleaning composition formed into moulded bodies for use in for example fabric washing, dishware washing, stain removal and water softening incorporates disintegrant granules comprising a water insoluble inorganic material and a water-swelling agent which,  
5 in its anhydrous state, comprises no more than 20 % of the combined weight of said inorganic material.

FOR UTILITY/DESIGN  
CIP/PCT NATIONAL/PATENT  
ORIGINAL/SUBSTITUTE/SUPPLEMENTAL  
DECLARATIONS

RULE 63 (37 C.F.R. 1.63)  
DECLARATION AND POWER OF ATTORNEY  
FOR PATENT APPLICATION  
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

PM&S  
FORM

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name, and I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the INVENTION ENTITLED CLEANING COMPOSITIONS

the specification of which (CHECK applicable BOX(ES))  
X -> ☒ is attached hereto  
BOX(ES) -> ☐ was filed on \_\_\_\_\_ as U.S. Application No. 0 / \_\_\_\_\_  
-> ☐ was filed as PCT International Application No. PCT/GB00/02785 on 24 July 2000  
-> ☐ and (if U.S. or PCT application amended) was amended on \_\_\_\_\_  
I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 C.F.R. 1.56. I hereby claim foreign priority benefits under 35 U.S.C. 119/365 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate filed by me or my assignee disclosing the subject matter claimed in this application and having a filing date (1) before that of the application on which priority is claimed, or (2) if no priority claimed, before the filing date of this application

| PRIOR FOREIGN APPLICATION(S)        | Date first laid-open or Published | Date Patented or Granted | Priority Claimed |
|-------------------------------------|-----------------------------------|--------------------------|------------------|
| Number Country Day/MONTH/Year Filed |                                   |                          | Yes No           |
| 9918782.5 GB 10 August 1999         |                                   |                          |                  |

I hereby claim domestic priority benefit under 35 U.S.C. 119/120/365 of the indicated United States applications listed below and PCT international applications listed above or below and, if this is a continuation-in-part (CIP) application, insofar as the subject matter disclosed and claimed in this application is in addition to that disclosed in such prior applications, I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 C.F.R. 1.56 which became available between the filing date of each such prior application and the national or PCT international filing date of this application:

| PRIOR U.S. PROVISIONAL, NONPROVISIONAL AND/OR PCT APPLICATION(S) | Status                       | Priority Claimed |
|--|------------------------------|------------------|
| Application No. (series code/serial no.) Day/MONTH/Year Filed    | pending, abandoned, patented | Yes No           |
| PCT/GB00/02785 24 July 2000                                      |                              |                  |

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

And I hereby appoint Pillsbury Madison & Suto LLP, Intellectual Property Group, 1100 New York Avenue, N.W., Ninth Floor, East Tower, Washington, D.C. 20005-3918, telephone number (202) 861-3000 (to whom all communications are to be directed), and the below-named persons (of the same address) individually and collectively my attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith and with the resulting patent, and I hereby authorize them to delete names/numbers below of persons no longer with their firm and to act and rely on instructions from and communicate directly with the person/assignee/attorney/firm/organization who/which first sends/sent this case to them and by whom/which I hereby declare that I have consented after full disclosure to be represented unless/until I instruct the above firm and/or a below attorney in writing to the contrary

|                            |                         |                          |                            |
|----------------------------|-------------------------|--------------------------|----------------------------|
| Paul N. Kokulis 16772      | Donald J. Bird 25323    | Lynn E. Eccleston 35861  | Roger R. Wise 31204        |
| Raymond F. Lippitt 17519   | Peter W. Gowdey 25872   | David A. Jakopin 32995   | Jay M. Finkelstein 21082   |
| G. Lloyd Knight 17698      | Dale S. Lazar 28872     | Mark G. Paulson 30793    | Antia M. Kirkpatrick 32617 |
| Carl G. Love 18781         | Glenn J. Perry 28458    | Timothy J. Klima 34852   | Michael R. Dzwonczyk 32456 |
| Kevin H. Martin 20534      | Kendrew H. Colton 30368 | Stephen C. Glasier 31361 | W. Patrick Bengtsson 37087 |
| William K. West, Jr. 22877 | P. E. White, Jr. 32011  | Paul F. McQuade 31342    | Jack S. Barufka 41835      |
| Edgar E. Joyce 20508       | Ruth N. Morduch 21044   | Adam R. Hess 27248       |                            |
| George M. Sirila 18221     | G. Paul Edgell 24238    | Richard H. Zaitlen 27248 |                            |

1. INVENTOR'S SIGNATURE: Michael Freaney Date 21st January 2002

Inventor's Name (typed) Michael First D Middle Initial FREANEY Family Name GB  
Residence (City) Warrington (State/Foreign Country)  
Post Office Address (Include Zip Code) 41 Moore Ave, Thelwall, Warrington, Cheshire WA4 2JN, UK GBX

2. INVENTOR'S SIGNATURE: M. Woodhouse Date 28th January 2002

Inventor's Name (typed) Mark First A Middle Initial WOODHOUSE Family Name GB  
Residence (City) Warrington (State/Foreign Country)  
Post Office Address (Include Zip Code) 40 Bishopdale Close, Whittle Hall, Warrington, Cheshire WA5 3DF, UK

3. INVENTOR'S SIGNATURE: Pieter Kreischer Date 31 Jan. 2002

Inventor's Name (typed) Pieter First H Middle Initial KREISCHER Family Name NL  
Residence (City) Maastricht (State/Foreign Country)  
Post Office Address (Include Zip Code) Karpothegge 35, 6225 KJ Maastricht, Netherlands NL

(FOR ADDITIONAL INVENTORS, check box ☐ and attach sheet (PAT-116.2) for same information for each re signature, name, date, citizenship, residence and address.)